Status of
Hg^0 and $HgCl_2$ and HCl Reference Gas Standards

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Presentation Overview

- The problem with elemental and oxidized Hg reference gas standards
- Joint EPA/NIST study on oxidized Hg reference gas measurement quality
  - The NIST approach for low uncertainty reference gas standard measurements
  - EPA's approach to develop low uncertainty measurement capabilities
  - Applying these techniques to measure the output of evaporative $HgCl_2$ generators
- Update on Hg^0 and HCl gas standards

Status of Oxidized Hg Reference Gases

$Hg^0 \neq HgCl_2$

- Early Hg CEM demonstration studies found that NIST-traceable Hg^0 generators and evaporative $HgCl_2$ reference gas generators did not agree
  - ~7-10% differences have been observed
  - Many reasons suggested for this discrepancy
- The Traceability Protocol for Oxidized Hg Generators allows a “correction factor” to make them functionally agree

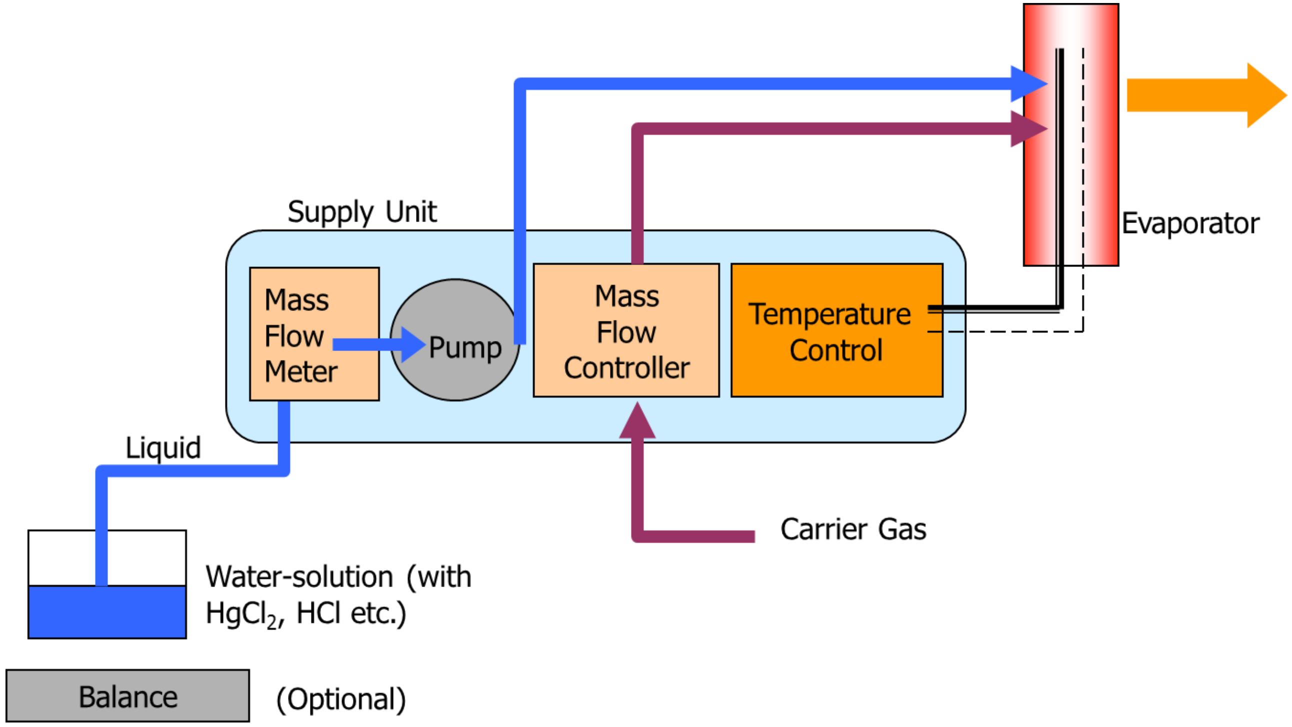
Status of Oxidized Hg Reference Gases

$Hg^0 \neq HgCl_2$

- Currently, evaporative $HgCl_2$ reference gases are not accepted as the same quality as Hg^0 reference gas standards and cannot be used for emissions quantitation
- Appendix A of MATS Rule now prohibits use of $HgCl_2$ gases for daily checks:

  "5.1.2.1 Calibration error tests of the Hg CEMS are required daily, except during unit outages. Use a NIST-traceable elemental Hg gas standard for these calibrations. If your Hg CEMS lacks an integrated elemental Hg gas generator, you may continue to use NIST-traceable oxidized Hg gases for the 7-day calibration error test (or the daily calibration error check) until such time as NIST-traceable compressed elemental Hg gas standards, at appropriate concentration levels, are available from gas vendors.
- NIST-traceable $HgCl_2$ reference gases of the same functional quality as NIST-traceable Hg^0 reference gases remains the ultimate goal
- NIST and EPA are collaborating to investigate the discrepancy

$HgCl_2$ Evaporative Generators



Traceability for Evaporative $HgCl_2$ Generators

- EPA Traceability Protocol for Qualification and Certification of Oxidized Mercury Gas Generators http://www3.epa.gov/ttn/emc/metals/OxHgProtocol.pdf
- The NIST-traceable concentration and associated uncertainty is theoretical, not measured
- Based on the following components:
  - Working solution concentration
  - Liquid feed rates
  - Carrier gas flow rate
- Traceability and uncertainty of working feed solution established by use of commercially available NIST-traceable $HgCl_2$ liquid standards
- Traceability and uncertainty of liquid feed rates established by gravimetrically calibrating the feed rate meter using a balance and NIST- traceable weights
- Traceability and uncertainty of carrier gas flow established by comparison with NIST- traceable reference standard flow measurement device
- Calculations provided to determine combined, expanded uncertainty of the generated concentrations
- **The theoretical concentration is NOT empirically verified**

Scientific Premise

- NIST Standard Reference Material (SRM) 3133 is ***the*** common denominator Hg reference material
  - SRM 3133 traceable solution used to analyze NIST prime certification sorbent traps
  - SRM 3133 traceable $HgCl_2$ feed solution used for evaporative generators
  - SRM 3133 traceable calibration solution used for Method 30B trap analysis
- ***In theory****, Hg^0 and $HgCl_2$ evaporative generators should agree at identical concentrations as both tied to SRM 3133*
- ***In theory****, Method 30B trap analyses should agree with NIST trap analyses as both analyses tied to SRM 3133*
- NIST and EPA collaborating to investigate these theories

Research Objectives

- ***Revisit the Hg^0 generator – $HgCl_2$ evaporative generator discrepancy issue***
- Accurately measure the output from NIST-certified Hg^0 and NIST-traceable evaporative $HgCl_2$ generators and quantitatively determine the difference(s), if any …
- Quantitatively compare NIST's sorbent trap analytical approach with the conventional Method 30B thermal sorbent trap analytical approach used for Hg emissions regulatory compliance
- Ultimate goal is to demonstrate acceptable, low uncertainty measurement capabilities applicable to ***both*** Hg^0 generators and $HgCl_2$ evaporative generators
- Can the conventional 30B thermal analysis approach be a suitable verification tool?

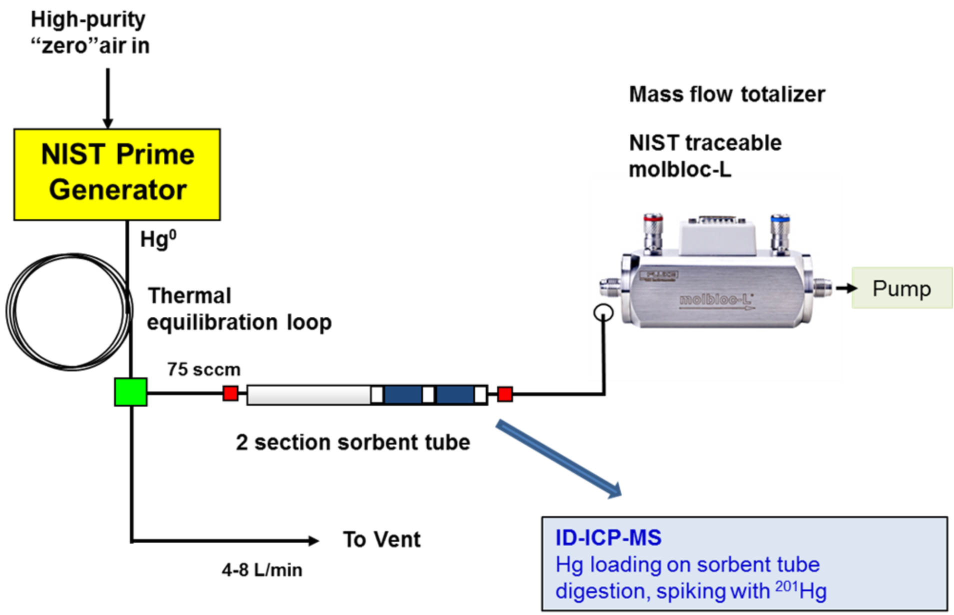
NIST Sorbent Trap Loading System

- Approach used to certify NIST Prime Hg^0 generators for regulatory reference gases:

- Based on EPA Method 30B:
  -Iodated carbon sorbent traps

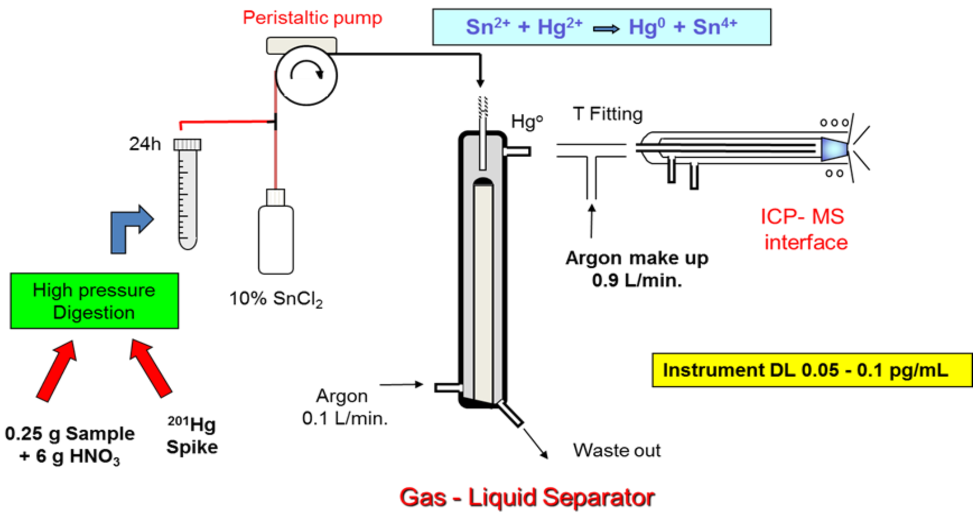
- Traps suitable for multiple analytical approaches:

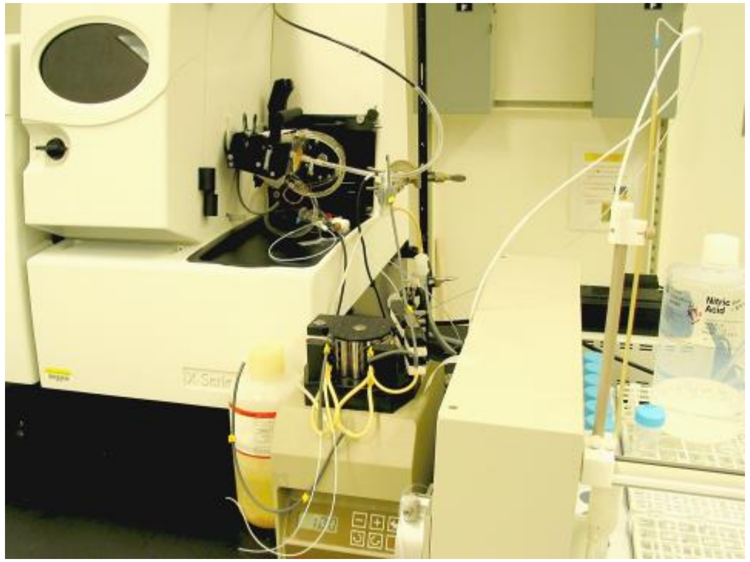
- Low uncertainty total sample volume:
  ~0.3 % U



NIST Isotope Dilution - ICP-MS Method

- Analytical Blank:
  Extremely low, 5-10 pg
- Repeatability:
  0.1 % - 0.3 %
- Memory Effects:
  Low
- Quantitation Limit:
  Approximately 20 pg/g in any matrix
- Matrix Effects:
  None; No need to use large dilution factors
- Sample Throughput:
  Instrument throughput 10 - 20 samples/hour
- Uncertainty:
  ~1%
- Combined measurement uncertainty:
  ~2%





EPA Sampling and Analytical Systems

- EPA's sampling system very similar to NIST's:
  - Alicat MFM for total sample volume
  - Includes moisture removal
  - All components heated to sampling point
  - Nominal Hg sample loading 100 ng
  - Sampling volume uncertainty ~0.5%
- Ohio Lumex Thermal Analysis System:
  - Direct combustion of carbon material
  - Calibration by Hg solution
  - 100 ng Hg nominal calibration mass
  - Analytical uncertainty ~2%
- Combined measurement uncertainty ~3%

Experimental Approach

- Measure the outputs from a NIST-certified Hg^0 generator and a NIST-traceable $HgCl_2$ evaporative generator
- Low uncertainty sorbent trap sampling followed by NIST's low uncertainty isotope dilution – inductively coupled plasma mass spectrometry (ID-ICPMS) analysis *and* EPA's Method 30B thermal analysis

Initial Experiments

- Optimize EPA thermal analysis approach:
  - Calibration volume
  - Calibration solution (3133 or 3177?)
- Verify analytical agreement of 3133 and 3177 Hg SRMs:
  - Direct liquid calibration
  - Spike each SRM solution in $SnCl_2$ sparger to result in Hg^0 on traps
- EPA analyze NIST Prime Hg^0 generator trap samples by thermal technique
- Collect sorbent trap samples from NIST-traceable, $HgCl_2$ evaporative generator
  - HovaCAL evaporative generator
  - $HgCl_2$ feed solution from 3177 SRM
  - 100 ng Hg target mass
- Spike additional $SnCl_2$/Hg^0 traps
- Distribute traps to NIST and EPA for analysis

Results and Discussion

- EPA tests to optimize thermal analysis approach:
  - All measurements based on fixed nominal 100 ng target mass
    - All quantitation based on area counts/ng
  - Compared 20 µl and 100 µl liquid injections (3133 and 3177 SRMs)
    - 20 µl better to calibrate with than 100 µl (precision)
    - Bias observed between 3133 and 3177 SRM responses (3177 3-4% lower)
  - All calibrations going forward based on 20 µl (100 ng) injections of 3133 solution
- EPA tests to quantitatively compare 3133 and 3177 SRMs:
  - Measured 3133 and 3177 solutions as Hg^0
    (20 µl and 100 µl liquid injections through $SnCl_2$)
    - 100 µl performed better (precision)
  - Excellent agreement between 3133 and 3177 SRMs
    - 3133 recovery 99.3%
    - 3177 recovery 100.0%
- 3133 and 3177 SRMs functionally agree
- Negative bias associated with thermal analysis of $HgCl_2$ solution

Results and Discussion

Comparison of EPA and NIST analytical approaches

- EPA analyzed traps from NIST Prime Hg^0 generator
  - Traps sampled by NIST during NIST Prime certification
  - Traps analyzed by EPA with thermal system
- **EPA measured value 99.8% of expected value** (expected value based on NIST ID/ICP-MS approach)
- NIST analyzed SRM 3133 Hg^0 traps
  - Traps prepared by EPA
- **NIST measured value 99.3% of expected value**

Demonstrates fundamental agreement between analytical techniques for Hg^0

Results and Discussion

NIST-traceable $HgCl_2$ evaporative generator trap measurements

- HovaCAL run with SRM 3177 solution
- Traps sampled by EPA
- Traps analyzed by NIST and EPA
- **NIST measured value 101.0% of expected value**

NIST measured value confirms NIST-traceable theoretical concentration

- **EPA measured value 95.2% of expected value**

EPA thermal analysis technique currently not suitable for $HgCl_2$ trap measurements

Preliminary Study Conclusions

- NIST's low uncertainty, gaseous Hg measurement approach provides a valuable tool for absolute measurement of Hg^0 *and* $HgCl_2$
- **NIST's gaseous Hg measurement approach confirms the theoretical output of evaporative $HgCl_2$ generators**
- This output **agrees** with the current output of NIST-traceable Hg^0 generators

$$Hg^0 = HgCl_2$$

- While EPA's analytical approach is in agreement with NIST's for Hg^0, it appears there is a negative bias with EPA's analytical approach for $HgCl_2$
- EPA's low uncertainty measurement approach may be useful for Hg^0 generator QA/QC measurements

What's next …

- Hg^0 and $HgCl_2$ gases of the same functional quality is the ultimate goal
  - Uncertainties ≤ 5%, based on measured, not theoretical, output
- EPA and NIST plan to perform more comprehensive HovaCAL tests and include a Tekran 3315 $HgCl_2$ evaporative generator
- We also want to obtain a NIST-certified Vendor Prime to confirm certified Hg^0 values by NIST and EPA measurement approaches
- We also intend to explore other options for confirming the output of $HgCl_2$ evaporative generators
- Is there a need to demonstrate agreement on a Hg CEMS?

Status of Hg^0 Reference Gases

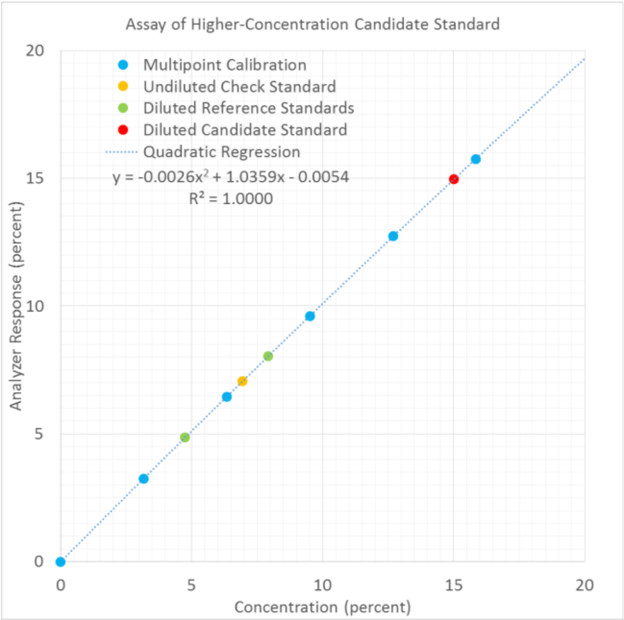
- NIST providing routine Hg^0 generator services
  - Hg CEMS vendors
  - Utilities/Hg CEMS integrators
  - Gas vendors
- Recent NIST Prime re-certifications
- NIST working on a new measurement approach
- Gas Manufacturers Alternative Certified Standards (GMACS) Hg^0 cylinders are now available

Status of HCl Reference Gases

- What's currently available are GMACS
- Available from multiple vendors
- NIST about to release a group of RGMs to multiple vendors
- HCl Protocol gases will again be available

Green Book Revisions? …

- EPA working on several Green Book issues
- Mostly minor changes (e.g., updates to Tables 2-2, 2-3, etc)
- Demand for additional gases
- Dilution approach for high level Protocol gases still a need
  - Procedure for diluting Protocol candidate to level comparable to available RGMs/NTRMs
  - Expands working ranges of Protocol gases
- A formal revision is not imminent



Link to Green Book questions:

www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards

Questions …

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